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(54) Title: SELECTIVE NON-CATALYTIC REDUCTION (SNCR) OF TOXIC GASEOUS EFFLUENTS IN AIRBAG INFLATORS

(57) Abstract

NH_2 radical-generating compounds, independent of the gas generant composition, reduce the toxicity of effluent gases produced by combustion of nonazide gas generating compositions used to inflate vehicle occupant restraint systems. By selective reactive of the NH_2 radical with NO in the combustion gas, N_2 is formed thereby decreasing the concentration of toxic nitrogen oxides therein. Placement of the reducing compounds proximate to the gas generant bed ensures intimate contact with the combustion gases, and yet still provides a noninvasive method of toxic gas reduction.

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SELECTIVE NON-CATALYTIC REDUCTION (SNCR) OF TOXIC GASEOUS EFFLUENTS IN AIRBAG INFLATORS

BACKGROUND OF THE INVENTION

The present invention relates generally to inflatable occupant safety restraints in motor vehicles, and more particularly to reducing the toxicity of effluent gases produced by nonazide gas generating compositions.

Inflatable occupant restraint devices for motor vehicles have been under development worldwide for many years, including the development of gas generating compositions for inflating such occupant restraints. Because the inflating gases produced by the gas generants must meet strict toxicity requirements, many gas generants now in use are based on alkali or alkaline earth metal azides, particularly sodium azide. When reacted with an oxidizing agent, sodium azide forms a relatively nontoxic gas consisting primarily of nitrogen.

However, azide-based gas generants are inherently volatile to handle and entail relatively high risk in manufacture and disposal. More specifically, whereas the inflating gases produced by azide-based gas generants are relatively nontoxic, the metal azides themselves are conversely highly toxic, thereby resulting in extra expense and risk in gas generant manufacture, storage, and disposal. In addition to direct contamination of the environment, metal azides also readily react with acids and heavy metals to form extremely sensitive compounds that may spontaneously ignite or detonate.

In contradistinction, nonazide gas generants, such as those disclosed in U.S. Patent No. 5,139,588 to Poole, typically comprise a nonazide fuel selected from the group of tetrazole compounds and metal salts thereof, and provide significant advantages over azide-based gas generants with respect to toxicity related hazards during manufacture and disposal. Moreover, most nonazide gas generant compositions typically supply a higher yield of gas (moles of gas per gram

of gas generant) than conventional azide-based occupant restraint gas generants.

However, many nonazide gas generants heretofore known and used produce high levels of toxic substances upon combustion. The most difficult toxic gases to control are the various oxides of nitrogen (NO_x) and carbon monoxide (CO). Because the gas generant of the passenger-side airbags is generally four times greater than that of the driver-side, the need for NO_x and CO reduction is most keenly felt when designing passenger-side airbags, although the concern exists for other airbag systems within the vehicle as well.

Reduction of the level of toxic NO_x and CO upon combustion of nonazide gas generants has proven to be a difficult problem. For instance, manipulation of the oxidizer/fuel ratio only reduces either the NO_x or CO. More specifically, increasing the ratio of oxidizer to fuel minimizes the CO content upon combustion because the extra oxygen oxidizes the CO to carbon dioxide. Unfortunately, however, this approach results in increased amounts of NO_x. Alternatively, if the oxidizer/fuel ratio is lowered to eliminate excess oxygen and reduce the amount of NO_x produced, increased amounts of CO are produced.

One way to improve the toxicity of the combustion gases is to reduce the combustion temperature which would reduce the initial concentrations of both CO and NO_x. Although simple in theory, it is difficult in practice to reduce the combustion temperature and to also retain a sufficiently high gas generant burn rate for practical application in an inflatable vehicle occupant restraint system. The burn rate of the gas generant is important to insure that the inflator will operate readily and properly. As a general rule, the burn rate of the gas generant decreases as the combustion temperature decreases. By using less energetic fuels, specifically fuels which produce less heat upon combustion, the combustion temperature may be reduced but the gas generant burn rate is also reduced.

Therefore, a need still exists for reducing the toxicity of effluent gases produced by nonazide gas generants without compromising the gas generant properties.

SUMMARY OF THE INVENTION

The aforesaid problems are solved, in accordance with the present invention, by a nonazide gas generating composition which in and of itself is nontoxic, and which upon combustion, also produces inflating gases that have reduced levels of NO_x and CO due to the use of a compound that generates NH_2 radicals in the gas phase. Selective non-catalytic reduction (SNCR) employs an NH_2 radical that selectively reacts with nitrogen oxide (NO) in the gas phase to form non-toxic nitrogen gas (N_2). In an SNCR system, basic requirements for the reduction of NO by an SNCR chemical include a well-mixed minimal 1:1 ratio of NH_2 radical to NO, whereby the NH_2 radical is generated by the SNCR chemical and the NO is generated from the gas generant combustion. Furthermore, the NH_2 radical must react for a sufficient residence time at a temperature within the range of 850-1150°C. The reduced content of toxic gases, such as NO_x and CO, allows the use of nonazide gas generants in vehicle occupant restraint systems while protecting the occupants of the vehicle from exposure to toxic gases which heretofore have been produced by nonazide gas generants.

More specifically, the present invention comprises a nonazide gas generant composition, and a separate NO_x reducing agent (SNCR) chemical that liberates NH_2 radical upon thermal decomposition and/or reaction with O_2. The NO_x gases generated from the combustion of the gas generant, such as NO and NO_2, selectively react with the NH_2 radicals, or NH_3 and O_2, thereby producing a harmless gas of N_2. A corresponding reduction in CO is an incidental benefit with the use of some of the reducing agents, such as $(NH_4)_2SO_4$. In addition, the chemistry of the SNCR chemical is noninvasive and will not interfere with the expected performance or stability of a gas generant combustion.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

In accordance with the present invention, a vehicle occupant restraint device utilizing an SNCR system comprises a gas generant and a de-NO_x agent. The de-NO_x agent is disposed around the periphery of the gas generant within the gas generant bed and is selected from a group including amides and imides, ammonium compounds, amine compounds, or any compound which produces an NH_2 radical in the gas phase. Examples of ammonium compounds include ammonium hydroxide (NH_4OH), ammonium carbonate ($(NH_4)_2CO_3$), ammonium sulfate ($(NH_4)_2SO_4$), ammonium chloride (NH_4Cl), ammonium carbamate ($H_2NCO_2NH_4$), and ammonium fluoride (NH_4F). Examples of amide and imide compounds, respectively, compounds are urea (H_2NCONH_2) and cyanuric acid ($(HNCO)_3$). Given the aforementioned benefits, the gas generant is preferably nonazide, although other gas generants such as an azide-based composition may be utilized in conjunction with SNCR. The SNCR chemical is preferably ammonium sulfate ($(NH_4)_2SO_4$) based on the optimum and unexpected results given in Example 3 below. Not only does $(NH_4)_2SO_4$ inhibit production of toxic NO_2, it actually reduces NO_2 over time. In general, ammonium compounds will generate the highest yield of NH_2 radicals.

SNCR is well known and commonly used in industrial boilers to decrease the levels of toxic nitrogen oxides. Until now, SNCR technology has not been successfully implemented in automotive airbag systems. NO is reduced to N_2 by the following gas phase reaction with an NH_2 radical:

$$NH_2 + NO \rightarrow N_2 + H_2O \qquad (1)$$

Because NO_2 is generated by NO, a reduction in NO necessarily causes an overall NO_x reduction within the inflator gas. The critical parameters for the successful implementation of SNCR in any system are the reaction temperature, NH_2 radical/NO ratio, mixing, residence time, and initial NO level. In

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addition, the presence of oxygen (O_2) is critical when the SNCR chemical is ammonia or an ammonium compounds.

To obtain NH_2 radical in the gas phase at the correct level, the SNCR chemical must thermally decompose to generate the NH_2 radical or NH_3 (which must subsequently react with O_2 to form the NH_2 radical). The decomposition products determine how much of the NH_2 radical is generated in the gas phase versus what is liberated directly from the SNCR chemical. The minimum NH_2 radical/NO ratio in the gas phase reaction should be 1 mole of NH_2 radical for each mole of NO. In general, a small excess of the NH_2 radical will simply result in the formation of small amounts of NH_3 and provide minimal additional NO reduction. SNCR technology is most effective at high initial levels of NO. When ammonium compounds are used, oxygen is necessary for the formation of NH_2 radicals, and should be present at levels of 0.1 to 11 volume percent.

The decomposition temperature, determinative of when NH_2 radicals are generated in the gas phase, is critical because the NH_2 radical must be "injected" into the gas phase at the correct temperature thereby enabling the selective reduction reaction of NO_x. For example, $(NH_4)_2SO_4$ decomposes at about 235°C while $(NH_4)_2CO_3$ begins to decompose at room temperature. During an inflator deployment, an SNCR chemical that decomposes at a lower temperature will be "injected" into the system sooner and, as illustrated in Example 4, provide a decreased reduction of nitrogen oxides. The importance of temperature is demonstrated by the following reactions:

$$NO + NH_3 + 1/4O_2 \rightarrow N_2 + 3/2H_2O \quad (2)$$

$$NH_3 + 5/4O_2 \rightarrow NO + 3/2H_2O \quad (3)$$

The desired reaction, (2), will only occur at a significant rate at temperatures above 850-950°C. However, at temperatures above 1050-1150°C, reaction (3) becomes dominant and undesirable NO is formed. In addition to temperature, the

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importance of good mixing and a sufficient residence time are obvious for the completion of any gas phase r action. Th gas temperatures, degree of mixing, and residence time for a given inflator are determined primarily by the gas generant properties and the inflator configuration and operating conditions.

The temperature of the gases in an inflator will generally vary from the hottest at the generant burning surface to the coolest at the inflator exit ports. Although temperature is extremely difficult to measure, variables such as the thermodynamic properties of the generant, the burning rate of the generant, the cooling devices within the inflator, and the operating pressure of the inflator each contribute to the overall operating temperature of the SNCR system. The residence time of the gases in an inflator is dependent on the presence of choked flow and the operating pressure. One skilled in the art will readily realize that cognizance and tailoring of these variables when choosing a gas generant will enable the use of a wide variety of gas generant compositions in conjunction with the SNCR system.

In accordance with the present invention, the SNCR chemical is a noninvasive composition whereby the normal combustion reaction of the gas generant is not interrupted or significantly altered. The present invention is illustrated by the following examples.

EXAMPLE 1

Two nonazide passenger inflators (NAPIs) with the same gas generant and hardware were built. Ammonium carbonate ($(NH_4)_2CO_3$) was added directly to the generant bed of one of the inflators as a powder at 1.4 wt% of the generant mass. The inflators were deployed in a 100 ft^3 tank and the gaseous effluents were measured over a 30 minute time period. Carbon monoxide (CO) and ammonia (NH_3) were measured by FTIR while nitrogen (II) oxide (NO), nitrogen (IV) oxide (NO_2), and total nitrogen oxides (NO_x) were measured by Chemiluminescence. The time weighted averag s are report d below in ppm.

Inflator	CO	NO	NO_2	NO_x	NH_3
Control	665	85.7	29.6	117.6	14
1.4% $(NH_4)_2CO_3$	705	52.8	0.9	53.6	96
Percent of Control	106%	62%	3%	46%	686%

This example illustrates that the addition of this SNCR ammonium salt significantly reduces the levels of toxic nitrogen oxides while leaving the CO essentially unchanged.

EXAMPLE 2

Two NAPIs with the same gas generant and hardware were built and tested as described in Example 1. However, the generant load and the cooling assembly differed from that used in Example 1. ($(NH_4)_2CO_3$) was added directly to the generant bed of one of the inflators as a powder at 2.6 wt% of the generant mass. The time weighted averages are reported below in ppm.

Inflator	CO	NO	NO_2	NO_x	NH_3
Control	822	106.1	50.5	162	16
2.6% $(NH_4)_2CO_3$	798	82.0	30.7	116	147
Percent of Control	97%	77%	61%	72%	919%

This example demonstrates the importance of choosing the correct inflator configuration for successful implementation of SNCR technology in an airbag inflator. In addition, this example shows that an excess of an SNCR chemical does not result in further NO_x reduction, but only in higher levels of NH_3 production.

EXAMPLE 3

Two NAPIs with the same gas generant and hardware were built and tested as described in Example 1. However, the generant load and the cooling assembly differed from that of Examples 1 and 2. $(NH_4)_2SO_4$ was added directly to the generant bed of one of the inflators as a powder at 1.2 wt % of the generant mass. The time weighted averages are reported below in ppm.

Inflator	CO	NO	NO_2	NO_x	NH_3
Control	437	59.6	12.5	73.3	8
1.2% $(NH_4)_2SO_4$	406	62.2	5.2	67.7	57
Percent of Control	93%	104%	42%	92%	712

Two quite unexpected, yet beneficial results were observed from these tests. First, the addition of ($(NH_4)_2SO_4$) resulted in a reduction of both NO_x and CO. Secondly, a comparison of the NO_2 evolution in the control and in the SNCR samples indicates a decline over time of the NO_2 species in the SNCR sample and an increase in the NO_2 species in the control sample. For the control inflator, the NO_2 was 9.4 ppm at 3 minutes and 16.4 ppm at 30 minutes. This is what is normally seen since the NO initially produced by the inflator slowly converts to NO_2 in the presence of O_2. For the inflator with the SNCR chemical, the NO_2 was 7.8 ppm at 3 minutes and steadily decreased to 5.0 ppm at 30 minutes. This example illustrates the effectiveness of this embodiment in retarding the generation of toxic NO_2, despite the presence of increased amounts of relatively nontoxic NO and O_2.

EXAMPLE 4

Four NAPIs with the same gas generant and hardware were built and tested as described in Example 1. However, the generant load and the cooling assembly differed from that used in Examples 1,2, or 3. $(NH_4)_2SO_4$ (decomposes at 235°C) and $H_2NCO_2NH_4$ (sublimes at 60°C) were each added directly to the generant bed of one of the inflators as a powder at 2.7 wt % of the generant mass. The time weighted averages are reported below in ppm.

Inflator	CO	NO	NO_2	NO_x	NH_3
Control	552	82.2	30.2	115.2	10
2.7% $(NH_4)_2SO_4$	453	81.5	6.2	66.2	105
2.7% $H_2NCO_2NH_4$	715	79	31	112.9	196

Again, the addition of $(NH_4)_2SO_4$ resulted in a reduction of NO_x and CO. Also, the NO_2 level went from 9.4 ppm at 3 minutes to 5.6 ppm at 30 minutes, verifying the data shown in Example 3. The decomposition and sublimation points of the different compounds are provided to demonstrate that the decomposition temperature must be considered as a critical factor to the success of the SNCR chemical.

While the preferred embodiment of the invention has been disclosed, it should be appreciated that the invention is susceptible of modification without departing from the scope of the following claims.

WE CLAIM:

1. A vehicle occupant restraint system comprising:
an inflatable air bag;
a gas generator;
a gas generant compound located within said gas generator; and
a selective non-catalytic reducing compound proximate to and interspersed about said gas generant compound, placed wherein said selective non-catalytic reducing compound is selected from the group comprising ammonium salts, ammonium hydroxide (NH_4OH), amine compounds, and amide and imide compounds.

2. A vehicle occupant restraint system of Claim 1 wherein:
said gas generant comprises a nonazide composition;
said ammonium salt is selected from a group consisting of ammonium hydroxide (NH_4OH), ammonium carbonate ($(NH_4)_2CO_3$), ammonium sulfate ($(NH_4)_2SO_4$), ammonium chloride (NH_4Cl), ammonium carbamate ($H_2NCO_2NH_4$), and ammonium fluoride (NH_4F); and
said amide compound is selected from a group consisting of urea (H_2NCONH_2); and
said imide compound is selected from a group consisting of cyanuric acid ($(HNCO)_3$).

3. A method of reducing the toxicity of effluent gases of a gas generator, used to inflate an airbag of a vehicle occupant restraint system, comprising the step of:

interspersing a selective n n-catalytic reducing compound about a gas generant composition within the gas generator; and

reacting with gaseous products of the selective non-catalytic reducing compound with the gaseous combustion products of the gas generant composition.

4. A vehicle occupant restraint system of Claim 1 wherein:

said gas generant compound consists of a nonazide composition; and

said selective non-catalytic reducing compound consists of an ammonium salt selected from a group consisting of ammonium carbonate ($(NH_4)_2CO_3$), ammonium sulfate ($(NH_4)_2SO_4$), ammonium chloride (NH_4Cl), ammonium carbamate ($H_2NCO_2NH_4$), and ammonium fluoride (NH_4F).

5. A vehicle occupant restraint system of Claim 1 wherein:

said gas generant compound consists of a nonazide composition; and

said selective non-catalytic reducing compound consists of urea (H_2NCONH_2).

6. A vehicle occupant restraint system of Claim 1 wherein:

said gas generant compound consists of a nonazide composition; and

said selective non-catalytic reducing compound consists of cyanuric acid ($(HNCO)_3$).

7. A vehicle occupant restraint system of Claim 1 wherein:

said gas generant compound consists of a nonazide composition; and

said selective non-catalytic reducing compound consists of ammonium hydroxide (NH_4OH).

8. A vehicle occupant restraint system of Claim 1 wherein:

said gas generant compound consists of a nonazide composition; and

said selective non-catalytic reducing compound consists of an amine compound.

9. The method of claim 3 wherein:

said selective non-catalytic reducing compound consists of an ammonium salt selected from a group consisting of ammonium carbonate ($(NH_4)_2CO_3$), ammonium sulfate ($(NH_4)_2SO_4$), ammonium chloride (NH_4Cl), ammonium carbamate ($H_2NCO_2NH_4$), and ammonium fluoride (NH_4F).

10. The method of claim 3 wherein:

said selective non-catalytic reducing compound consists of urea (H_2NCONH_2).

11. The method of claim 3 wherein:

said selective non-catalytic reducing compound consists of cyanuric acid ($(HNCO)_3$).

12. The method of claim 3 wherein:

said selective non-catalytic reducing compound consists of ammonium hydroxide (NH_4OH).

13. A vehicle occupant restraint system of Claim 1 wherein:

said selective non-catalytic reducing compound consists of an amine compound.